QUANTITATION/DETECTION LIMITS FOR THE ANALYSIS OF ENVIRONMENTAL SAMPLES

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I. INTRODUCTION

Analytical technology continues its unrelenting pace to develop methodology to lower the concentration limits at which the analytes can be measured. Picogram (10^{-12} grams) quantities are commonly reported as new detector systems for gas and liquid chromatography are developed. Advances in mass spectrometry are leading to lower levels of quantitation. For example, ion trap mass spectrometers and inductively coupled plasma-mass spectrometry (ICP-MS) are some highly sensitive techniques, which are becoming more commonly used for organic and elemental determinations respectively and capable of detecting subnanogram ($<10^{-9}$ gram) quantities. The statement following depicts the situation that we are encountering:

> "... the number of compounds detected in a sample of water is related to the detection level. As the detection level decreases an order of magnitude, the number of compounds detected increased an order of magnitude. Based on the number of compounds detected by current methods, one would expect to find every known compound at a concentration of 10^{-12} g/L or higher." - Dr. William T. Donaldson (EPA Athens Laboratory)

As the regulated community is required to perform within the level of increasingly restrictive compliance limits, the analytical chemist must emphasize to the public that all measurement data have an associated uncertainty interval(1). This information becomes critical as measurements are made approaching the lowest analytical capability of a given procedure.

II. ANALYTICAL LIMITS OF MEASUREMENT - DEFINITIONS

In their regulatory programs, the USEPA uses a variety of procedures to establish limits of measurement. In the following slide definitions are given to present an approach to define analytical capability.

<u>LIMIT OF DETECTION (LOD)</u> - Lowest concentration level that can be determined to be statistically different from a blank(7).

<u>METHOD DETECTION LIMIT (MDL)</u> - Minimum concentration of analyte that can be determined with 99% confidence that the true value is greater than zero(2,3,13).

<u>INSTRUMENT DETECTION LIMIT (IDL)</u> - Smallest signal above background noise that an instrument can detect reliably(7).

<u>LIMIT OF QUANTITATION (LOQ)</u> - Concentration above which quantitative results may be obtained with a specified degree of confidence(7).

<u>PRACTICAL QUANTITATION LIMIT (PQL)</u> - Lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operation conditions(5).

III. APPLICATION OF METHOD DETECTION LIMITS (MDL) SUBJECT TO MATRIX EFFECTS

The MDL is similar to the LOD except that the LOD is defined with a sample blank whereas the MDL is defined with either a blank or in each matrix being analyzed(2,3). In most cases, however, laboratories report MDLs determined at one point in time and routinely based on reagent water. They do not normally perform the MDL evaluation on the different matrices analyzed for regulations development, compliance monitoring, or tested to determine permit requirements.

In their proposal to set enforceable maximum contaminant levels (MCLs) for volatile synthetic organic chemicals in drinking water(5), EPA explains that the MDL could not be used as the basis for quantitative maximum contaminant levels: "The specification of such a concentration is limited by the fact that MDLs are variables affected by the performance of a given measurement system. MDLs are not necessarily reproducible over time in a given laboratory, even when the same analytical procedures, instrumentation, and sample matrix are used."

IV. PRACTICAL QUANTITATION LIMITS (PQL) AS A MEANS OF IDENTIFYING MEASUREABLE CONCENTRATIONS

Many observations for organic toxic pollutants are below the MDLs, thus creating difficulties in developing effluent limitations guidelines and permit limits. In such instances where analytical and effluent variability cannot be determined, only those concentrations above quantifiable levels (17) should be considered. It should also be recognized that there is a fundamental difference between detection and quantitation limits. Unfortunately these terms are too often misused as being synonymous. EPA has developed a method for establishing such quantifiable numerical limits for its proposed drinking water standards (50 FR 46902) and for its proposed organic toxicity characteristic (51 FR 21652), designated as the practical quantitation limit (PQL). EPA has developed this concept of a PQL for specific analytical methods and lists of chemicals.

A. RECOMMENDED PRACTICAL QUANTITATION LIMITS COMPARED TO METHOD DETECTION LIMITS

The EPA used PQLs which are recommended as 10 times the MDL for selected volatile organic chemicals when it proposed MCLs for drinking water. The Agency states that: "setting the PQLs in a range between 5 and 10 times the MDL achieved by the best laboratories is a fair expectation for most state and commercial laboratories" (50 FR 46907). At the PQLs chosen by EPA for this rulemaking, its performance evaluation studies indicate that 80% of the EPA and State laboratories in its water program evaluation studies could measure within ±40% of the true concentration. This was the basis for setting the PQL at 10 times the MDL. This is not a very high standard of performance as admitted by the Agency in the preamble to this proposed regulation. Thus, even at the PQLs, over 20% of the "good" laboratories would not be expected to obtain results within ±40% of the concentration of a specific component. At concentration levels below PQL, performance of even the best of "good" laboratories deterioriates rapidly.

B. PRACTICAL QUANTITATION LIMITS IN REAL MATRIX SAMPLES REFLECT EFFECT OF MATRIX INTERFERENCE

A recent presentation(12) described a study evaluating Method 8020, which is a gas/liquid chromatography procedure in SW-846 "Test Methods for Evaluating Solid Wastes, Physical Chemical Methods" for the determination of low concentrations of toluene, benzene, and xylenes in real matrix groundwater samples. The round robin study involved 20 commercial laboratories. Method 8020 lists the practical quantification limits for all three compounds as 2.0 μg/L. The PQLs derived from results achieved by the laboratories in this study are much higher. The PQLs at which 80% of the laboratories could achieve a recovery within ±40% of a true value from this study are 7.5 μg/L for benzene, >20 μg/L for toluene, and 18.5 μg/L for total xylenes. It is clear that the Method 8020 published PQLs are seriously underestimated when applied to this groundwater matrix and for these 20 laboratories.

The inability of these laboratories to perform within the method PQL criteria should not be surprising even to EPA. In the preamble to the final rule on the federal primary drinking water standards for eight volatile organic compounds (VOCs), EPA states that:

"PQLs for the VOCs were based on the MDL and surrogate test data ... The PQLs based on these laboratory data are considered a two step removed surrogate for actual laboratory performance, first because they are estimated from another measurement (the MDL) and second, because they are derived from laboratory performance under ideal circumstances. Therefore, they do not actually represent the results of normal laboratory procedures, but are a model of what normal procedures might achieve. Specifically:

(1) Laboratories receive performance evaluation samples in which a limited number of concentrations are analyzed and the samples do not have matrix interferences as might actual samples;

(2) PQLs are based on EPA and State laboratory data which are considered to be representative of the best laboratories, but not all laboratories; and

(3) Samples are analyzed under controlled ideal testing conditions which may not be representative of routine practices.

For these reasons, the PQL represents a relative stringent target for routine performance." (52 Federal Register 25699).

More specific to groundwater samples, EPA discussed the significance and reliability of the PQLs that are included in Appendix IX of the rule: "The PQLs listed were EPAs best estimate of the practical sensitivity of the applicable method for RCRA groundwater monitoring purposes. However, some of the PQLs may be unattainable because they are based on general estimates for the specific substance. Furthermore, due to site-specific factors, these limits may not be reached." 53 Federal Register 39721.

For solid wastes the matrix problem has also been demonstrated to be very significant(21). Member companies of the Hazardous Waste Treatment Council obtained initial information that showed 33 out of the 91 Best Demonstrated Available Technology (BDAT) standards promulgated for the First and Second Third Land Disposal Restrictions were set at levels below the PQLs. As a follow-up, a formalized interlaboratory study using incinerator ash samples was performed. In this matrix a range finder study was conducted by six member companies to determine appropriate spiking levels to determine MDLs for each of the constituents. As part of this study a matrix spike was prepared at the BDAT level and determined. The results of the study showed that 65 percent of the volatile constituents, 73 percent of the acid extractable constituents, and 23 percent of the base neutral extractable constituents were not detected at the spike performed at the treatment standard limit.

The PQLs and also MDLs published by EPA for its analytical methods are based on reagent water spiked with the compounds of interest, so they do not represent limits achievable where matrix interferences exist, as with actual samples. EPA does identify in Method 8020 that the PQLs are highly matrix-dependent and that they are listed only to provide guidance and may not always be achievable. Unfortunately, these caveats or warnings are likely to be ignored, particularly by some regulatory agencies, when permit limits or other regulatory levels are set.

V. PROPER TREATMENT OF THE DATA CAN AVOID MISREPRESENTATION OF THE FACTS

A. RULES FOR THE USE OF SIGNIFICANT NUMBERS

Despite the wide attention given to numbers for quantitative and qualitative limits the improper use of rules for use of significant numbers goes virtually unnoticed. As measurements are required more and more frequently to be made at decreasing concentrations, the relative analytical variability and uncertainty can increase substantially and the need to understand and recognize significant data is essential. Horwitz et al (22) reviewed data from over 50 independent Association of Official Analytical Chemists (AOAC) interlaboratory collaborative programs covering numerous AOAC drug and pesticide studies. The analytical methods covered were chromatography, atomic absorption spectrometry, absorption spectrometry, polarography, and biossay. In Figure 1 the % variation is expressed as powers of 2 with the mean concentration expressed as powers of 10. A convenient reference point is that at 1 ppm the variation is 16%. The % variation was found to double for each decrease of concentration by 2 orders of magnitude. It is important to note that this curve is independent of the analyte or analytical technique that was used to make the measurements. These relationships should also apply to environmental levels of measurement as well.

Analytical chemists must always emphasize to the users of the data that the single most important characteristic of any result obtained from one or more analytical measurements is an adequate statement of its uncertainty interval. Often in legal judgments there is an attempt to dispense with uncertainty and try to obtain unequivocal statements; therefore, an uncertainty interval must be clearly defined in cases involving litigation and/or enforcement proceedings. Otherwise, a value of 1.001 without a specified uncertainty, for example, may be viewed as legally exceeding a permissible level of 1(7).

The analytical inclusion of only significant numbers is vital to the accurate interpretation of data. Scientific personnel are not exempted from the tendency to retain all values, no matter how divergent or suspect they may be. One of the principles of handling the data of physical and chemical measurements is that a numerical result by itself should give an approximate idea of the precision of the value as indicated by the number of significant figures used in expressing the value. An inaccurate representation of significant figures may give one an impression nearly as erroneous as from an inaccurate value. Misuse of significant figures can cause reporting violations when indeed the measured value does not exceed the limit. Adherence to proper expression of significant numbers is especially important when permit limits are near the limit of quantitation for the procedure and its relative uncertainties are large.

The number of significant figures reported as a result of a scientific measurement depends on establishing previously the relative precision with which the measurement can be made as shown in Table II(11). In considering the proper use of significant figures for regulatory reporting, it is imperative that significant figures start at the laboratory bench and be adhered to by anyone who further treats or handles the data. Otherwise, false conclusions and misunderstanding will develop and possibly lead to serious consequences.

B. GUIDELINES FOR REPORTING DATA

EPA has recognized that data measured at or near the detection limit have considerably more uncertainty associated with them than when significant amounts are present(6). In this discussion EPA acknowledges the recommendations by the American Chemical Society Report(7). A graphical illustration of the relationship of LOD and LOQ is shown in Figure 2(7). The base scale is in units of standard deviation, which is assumed to be the same for all the measurements involved.

Confidence in the apparent analyte concentration increases as the analyte signal increases above the LOD. The value for LOQ = 10σ is recommended, where σ is the standard deviation of the measurements. Assuming a large number of samples, the LOQ then corresponds to an uncertainty of ±30% in the measured value ($10\sigma \pm 3\sigma$) at the 99% confidence level. The LOQ is most useful for defining the lower limit of the useful range of measurement methodology.

From these guidelines in Table III, if the measured value is less than the limit of detection, one should report "not detected" together with the value for the LOD. When the measured value is larger than the LOD but smaller than the limit of quantification (LOQ), report "detected but not quantifiable" together with the value for the LOQ. If the measured value is greater than the LOQ, report the value and its uncertainty.

VI. IMPACTING THE REGULATORY PROCESS

Data measured at or near the limit of detection may cause serious difficulty for the user in developing valid conclusions from any study. Not only can the amount of uncertainty approach and even equal the reported value, but also confirmation of the species reported is virtually impossible as the identification must depend solely on the selectivity of the methodology and knowledge of the absence of possible interferents. As the concentrations increase to measurable amounts these problems diminish. As stated previously, quantitative interpretation, decision-making, and regulatory actions should be limited to data at or above the limit of quantitation(7). The following discussion graphically illustrates how analytical variability can impact the regulatory process.

A. GRAPHICAL ILLUSTRATIONS OF THE IMPACT OF ANALYTICAL VARIABILITY ON COMPLIANCE LIMITS

Figures 3 through 7 were developed in order to visualize the impact of variability upon laboratory measurements of concentrations in plant effluents. Figure 3 shows the general probability distribution function for random error when the measured concentration is expressed in σ units. This curve can be thought of as a frequency distribution when a large number of effluent samples of the same concentration are analyzed repetitively. The x-axis is the concentration that a laboratory may measure; the y-axis is proportional to the frequency the laboratory measures a given concentration and is expressed in probability units. The y-axis data have been normalized so that the total area under the curve gives a value of 1.000. This curve applies to all analyses in which only random error occurs.

Several observations can be made regarding the probability distribution shown in Figure 3.

Observation #1: Only a small percentage of the total analyses may give the best estimate of the true value.

Observation #2: One-half the measurements are above the mean and one-half of the measurements are below the mean. Therefore, if the mean is some effluent trigger concentration above which a plant would be violating its permit, the plant would be failing one-half the time, if these data were treated as having no uncertainty.

Observation #3: The measured concentrations shown in Figure 3, 99.7% of the reported values would fall between plus or minus 3σ of the mean concentration; therefore, it can be seen that the σ of a determination is a very fundamental property of a distribution which must be used in evaluating data which contains uncertainty.

B. THE APPLICATION TO REGULATORY LIMITS

In order to translate this general probability distribution to real-world examples, Figures 4 through 7 were generated assuming different analytical uncertainty in the random errors. All figures were generated for the measurement of an effluent sample containing 100 μg/L of the target analyte. Figure 4 shows the distribution of measured concentrations when the analytical uncertainty produces a value of 1μg/L for σ; Figure 5 shows the distribution of measured concentrations when the analytical uncertainty produces a value of 10 μg/L for σ: Figure 6 shows the distribution of measured concentrations when the analytical uncertainty produces a value of 30 μg/L for σ; and Figure 7 shows the distribution of measured concentrations when the analytical uncertainty produces a value of 100 μg/L for σ. The probability distribution for the last case has been truncated at 0 μg/L since negative values of concentration are meaningless.

These four cases show clearly the impact of determinations which are carried out with different amounts of analytical uncertainty. Unfortunately, regulations are written as if data were being obtained with an uncertainty less than that shown in Figure 4. Permits which give a specific limit for a certain compound, fall into this category. However, the analytical data which are being obtained by a typical environmental laboratory for the analysis of reagent water are most likely analytical data obtained with the uncertainty shown in Figures 6 or 7. Figure 6 describes most analytical data obtained using EPA Methods 624 and 625 when the measured concentration is ten times higher than the method detection limit determined in reagent water. Figure 7 describes most analytical data obtained using EPA Methods 624 and 625 when the measured concentration is equal to the method detection limit which can be the case if the sample or sample extract must be diluted due to interfering substances. The concern is that the probability distribution summarized in Figure 6 is used by the Environmental Protection Agency to characterize data obtained by analytical laboratories for effluent analyses. However, these data represent a best case, since method detection limits for Methods 624 and 625 are derived from the analysis of reagent water. Reagent water data should not necessarily be used to determine the random error associated with all plant effluents which may contain relatively high levels of inorganic salts, and unregulated organic compounds which may interfere with these methods.

An additional important conclusion from this set of figures is that these case studies must be applied not only to analytical data obtained using the classical EPA Methods 624 and 625, but it also applies to BOD, COD, toxicity, opacity, etc. **Any time any measurement is being made which includes random error, this measurement contains the same types of uncertainty as described above which is certainly accentuated as the required concentration limits are decreased.** Therefore, regulations should not be written with wording that implies that Figure 4 uncertainties exist when in fact Figures 6 and 7 uncertainties are typical representations of analytical uncertainties associated with permit violation data.

Evaluation of permit violations cannot be properly made without first knowing the analytical uncertainty of the determination in the vicinity of the permit trigger concentrations and for the exact matrix under study. This means that σ data which are published with EPA Methods for the analysis in spiked reagent water should only be used as a guide. For application, however, this information should be developed for each compound/parameter in each laboratory performing these analyses.

C. THE APPLICATION TO BACKGROUND CONTAMINATION

As regulated limits go lower and lower, background contamination becomes an ever increasing problem. However, this topic can be treated in much the same way as were regulatory limits discussed above. The same analytical uncertainty must also be applied to the analysis of method blanks. In this case, method blanks are not defined as replicate injections of a sample extract, but are replicate extraction and extract analyses when representative glassware, solvents, instrumentation, etc. are used in the analyses. Using this same reasoning, an analysis of the mean concentration of the background contamination and the σ for that determination gives one the information needed to determine whether a measured quantity in a plant effluent sample is actually different from the quantity present in the method blank.

For commonly occurring background contaminants such as methylene chloride, acetone, toluene, 2-butanone, and common phthalates no positive sample results should be considered real which are within 10σ of the mean background concentration. All measured concentrations in all samples and method blanks should be reported, with qualifiers such as BBL (below background level) being used for those concentrations which are within 10σ of the blank concentration.

VII. RECOMMENDATIONS

There is a LOD or MDL which can be determined for every analyte in every matrix below which it is not possible to reliably ascertain that an analyte is present or absent. There is also a concentration range above the LOD or MDL where it is possible to qualitatively establish the presence of an analyte, but the concentration cannot be accurately and reliably quantified. It is also not practical to determine precisely the LOD or MDL for all analytes, in every matrix, and at all laboratories. All regulatory programs must recognize these facts. As a practical solution to this problem, every method should have published practical quantification limits (PQLs) which are at least media (water/soil) specific. Many of these PQLs have been published by media, and for most analytes these PQLs are representative of levels that can be achieved at most commercial laboratories. However, there should also be procedures for determining matrix specific detection and quantitation limits. Unfortunately it is not possible to analyze a large enough universe of matrices to establish generalized quantitation limits for comparison with regulatory levels. An approach must be established which will preserve the utility of published PQLs as guidance, while recognizing the significant number of compliance limits which are below their respective PQLs and thus require a variance procedure.

If a laboratory determines that it can not meet published detection and quantitation limits in their sample matrix, they should be allowed to measure these levels using established procedures which include mandated QA/QC requirements. These levels would then be used as reporting limits. If the quantitation limit, so established, is above the regulatory level, the compound would be considered to be in compliance until such a time that a level above the quantitation limit is measured. This assumption of compliance would apply whether or not the quantitation limit were a published PQL or a measured quantitation limit. EPA would also determine the frequency that these published PQLs would be re-evaluated pending method and equipment improvement. In some cases the Agency has suggested that a facility may petition for such a variance (24).

We also recommend that the EPA establish uniformity among the various regulatory programs for the determination of the method detection limit. Although the definition is essentially the same, the number of replicates and blanks may be different, therefore, the calculation is effected. This can further compound the current state of confusion in understanding and applying quantitation and detection limits. The corresponding quantitation limit should be established at five to ten times the MDL or substantially higher as the matrix would dictate (19). The use of such factors, however, must be used with extreme care as the method variability may well be underestimated by most laboratories (17). EPA recognized this need for consistency in its Report to Congress in CWA Section 518. It was reported that analytical methods are sometimes unnecessarily different for similar sample matrices, target analytes and data quality objectives. The Agency should move to greater method uniformity and more consistency in the use of quantitation and detection limits and use these concepts in regulatory compliance situations.

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"... THE NUMBER OF COMPOUNDS DETECTED IN A SAMPLE OF WATER IS RELATED TO THE DETECTION LEVEL. AS THE DETECTION LEVEL DECREASES AN ORDER OF MAGNITUDE, THE NUMBER OF COMPOUNDS DETECTED INCREASED AN ORDER OF MAGNITUDE. BASED ON THE NUMBER OF COMPOUNDS DETECTED BY CURRENT METHODS, ONE WOULD EXPECT TO FIND EVERY KNOWN COMPOUND AT A CONCENTRATION OF 10^{-12} G/L OR HIGHER."

DEFINITION OF ANALYTICAL CAPABILITY

- LIMIT OF DETECTION (LOD) – Lowest concentration level that can be determined to be statistically different from a blank.

- METHOD DETECTION LIMIT (MDL) – Minimum concentration of analyte that can be determined with 99% confidence that the true value is greater than zero.

- INSTRUMENT DETECTION LIMIT (IDL) – Smallest signal above background noise that an instrument can detect reliably.

- LIMIT OF QUANTITATION (LOQ) – Concentration above which quantitative results may be obtained with a specified degree of confidence.

- PRACTICAL QUANTITATION LIMIT (PQL) – Lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operation conditions.

(1) Laboratories receive performance evaluation samples in which a limited number of concentrations are analyzed and the samples do not have matrix interferences as might actual samples;

(2) PQLs are based on EPA and State laboratory data which are considered to be representative of the best laboratories, but not all laboratories; and

(3) Samples are analyzed under controlled ideal testing conditions which may not be representative of routine practices.

For these reasons, the PQL represents a relative stringent target for routine performance. (52 Federal Register 25699).

Comparison of Reportable Significant Figures as a Function of Relative Precision

Precision (%)	Significant Figures	Example Calculated	Example Reported
±0.001 to ±0.01	5	54.8149	54.815
±0.01 to ±0.1	4	54.8149	54.81
±0.1 to ±1	3	54.8149	54.8
± 1 to ±10	2	54.8149	55
± 10 to ±30	1	54.8149	5×10^1

ACS GUIDELINES FOR REPORTING DATA

Analyte Concentration in Units of σ $(S_t - S_b)$	Region of Reliability
<3	Region of questionable detection (and therefore unacceptable)
3	Limit of detection (LOD)
3 to 10	Region of less-certain quantitation
10	Limit of quantitation (LOQ)
>10	Region of quantitation

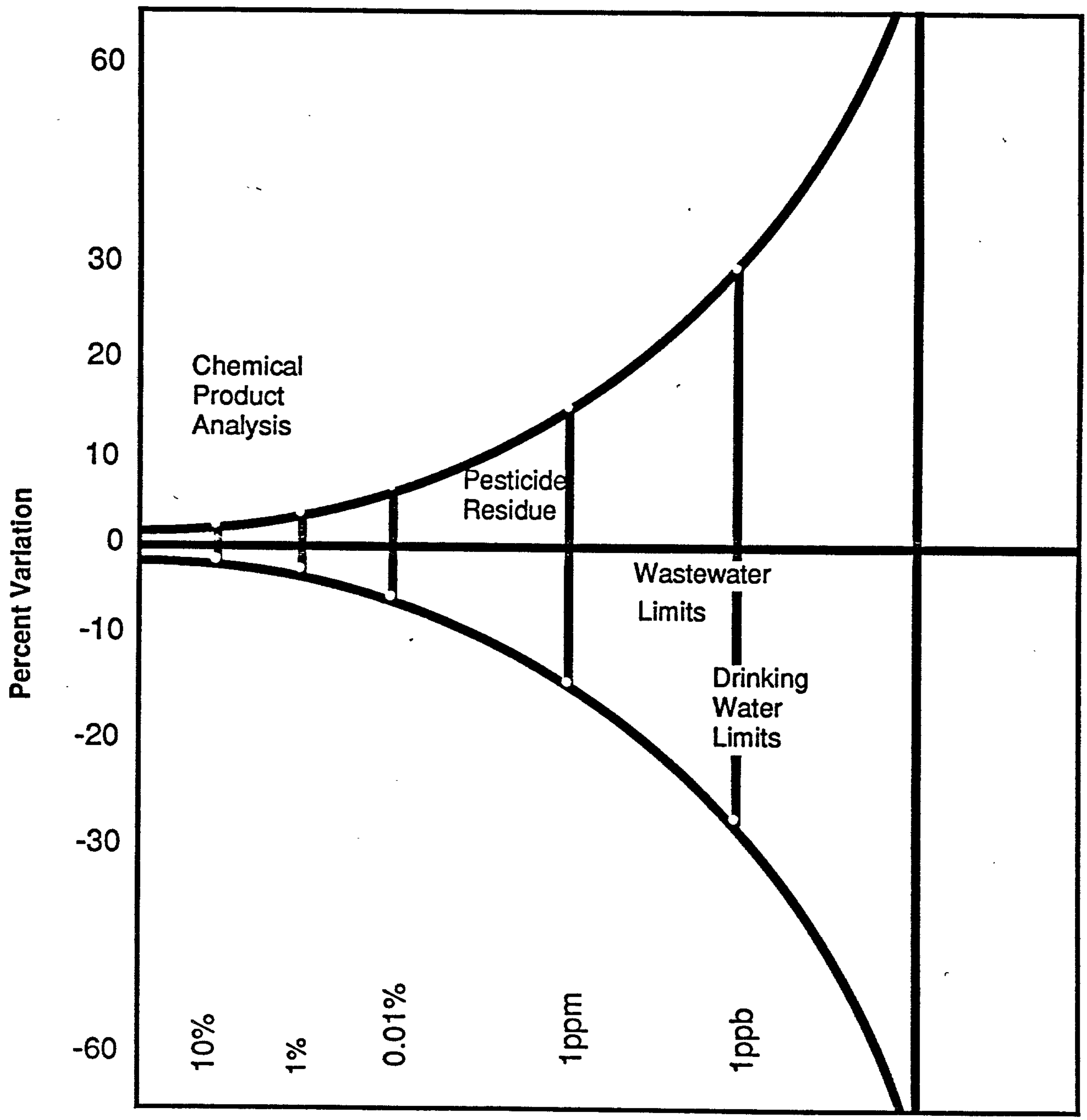

FIGURE 1. CURVE RELATING VARIABILITY BETWEEN LABORATORIES AND CONCENTRATION.

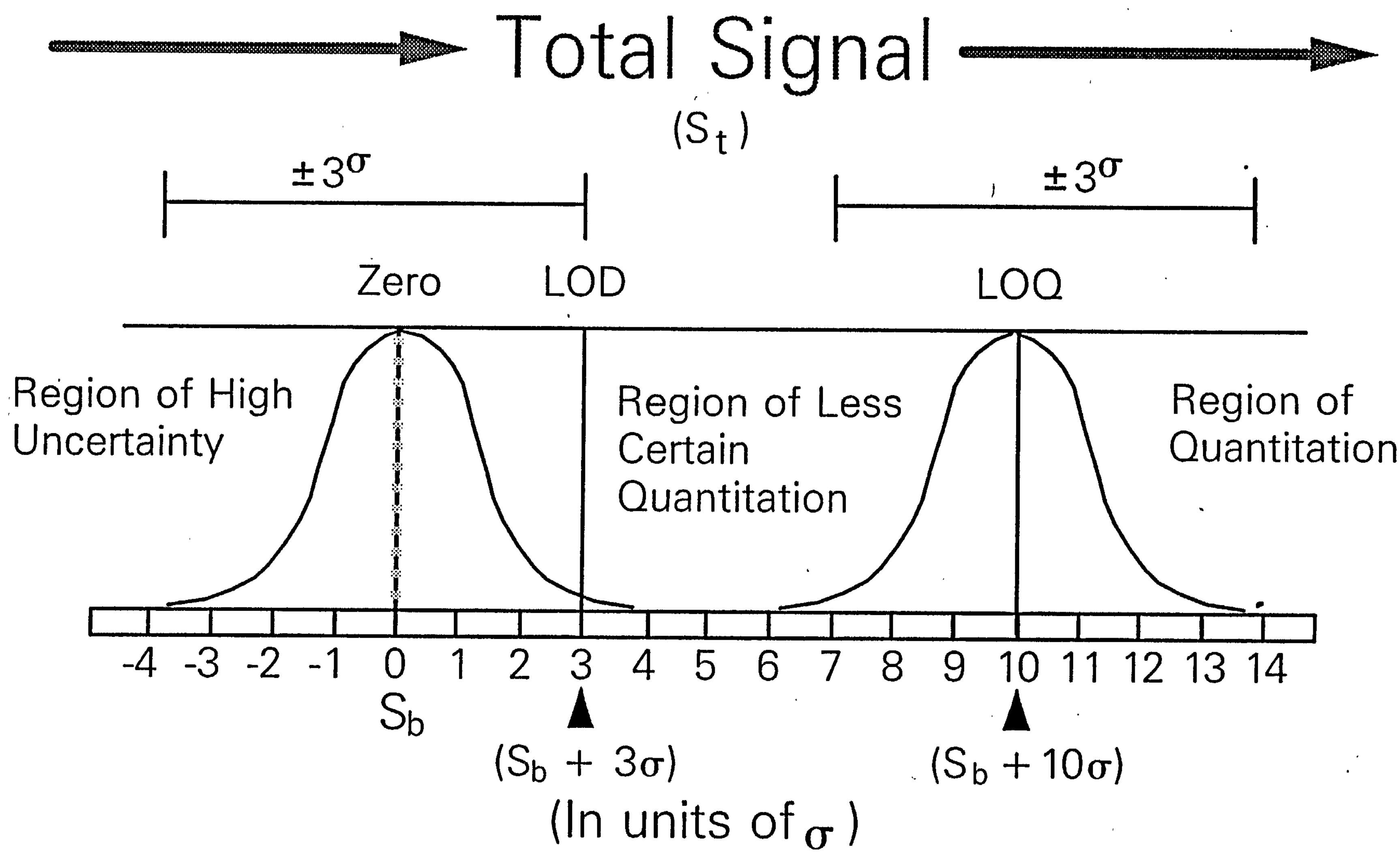

FIGURE 2, RELATIONSHIP OF LOD AND LOQ TO SIGNAL STRENGTH

Figure 3. Normal Curve of Random Error (x in sigma-units from mean)

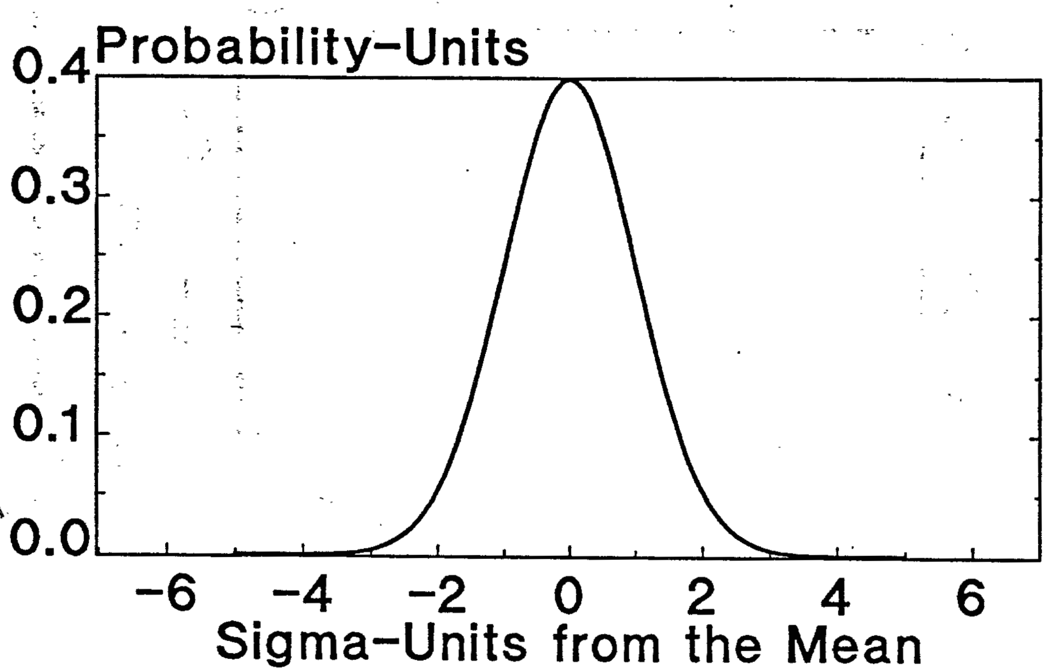

Figure 4. Normal Curve of Random Error
Mean = 100 ug/L; Sigma = 1 ug/L

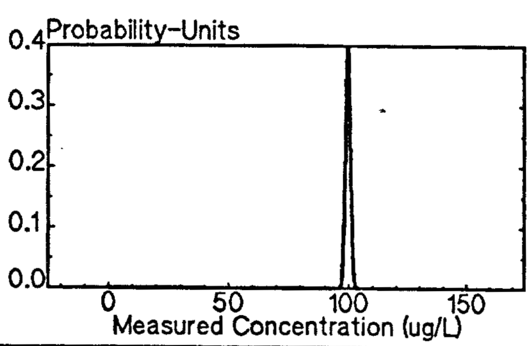

Figure 5. Normal Curve of Random Error
Mean = 100 ug/L; Sigma = 10 ug/L

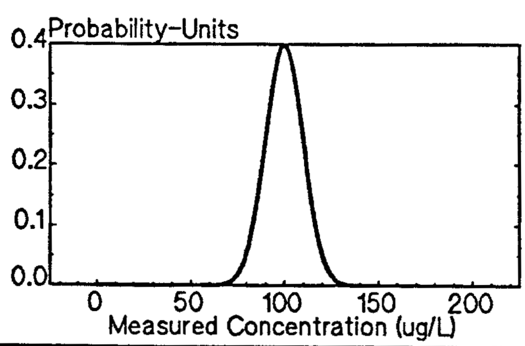

Figure 6. Normal Curve of Random Error
Mean = 100 ug/L; Sigma = 30 ug/L

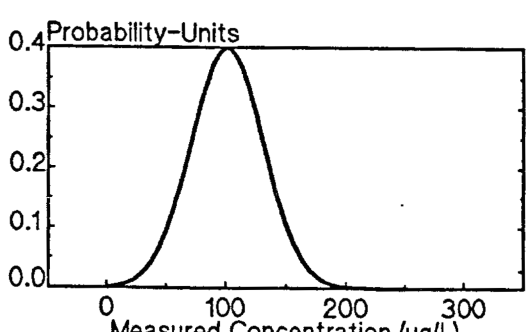

Figure 7. Normal Curve of Random Error
Mean = 100 ug/L; Sigma = 100 ug/L

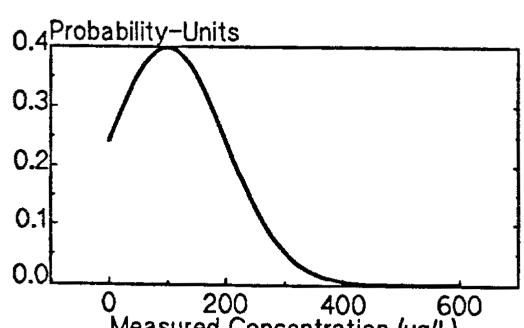

Figure 5. Normal Curve of Random Error
Mean = 100 ug/L; Sigma = 10 ug/L

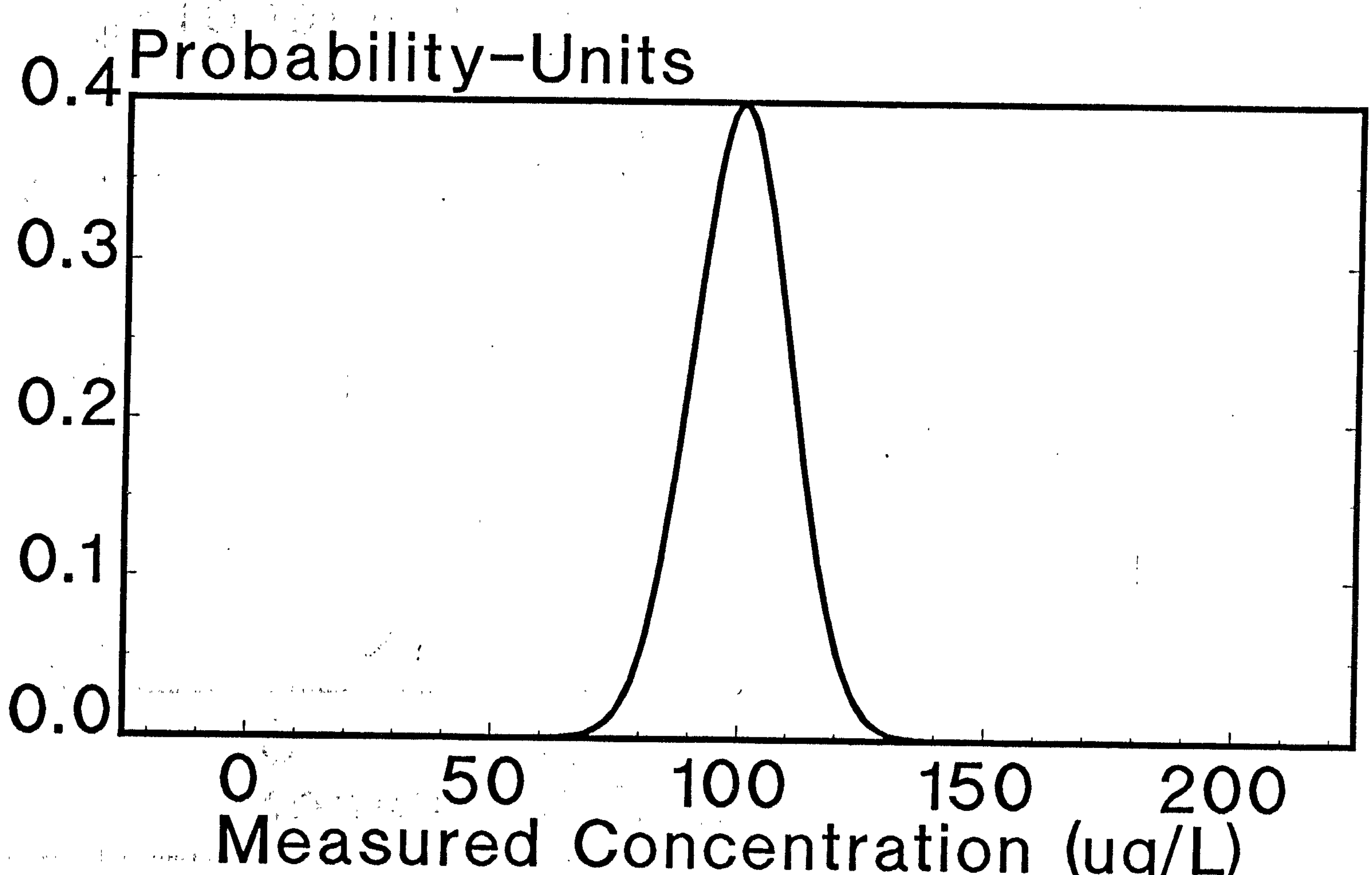

Figure 4. Normal Curve of Random Error
Mean = 100 ug/L; Sigma = 1 ug/L

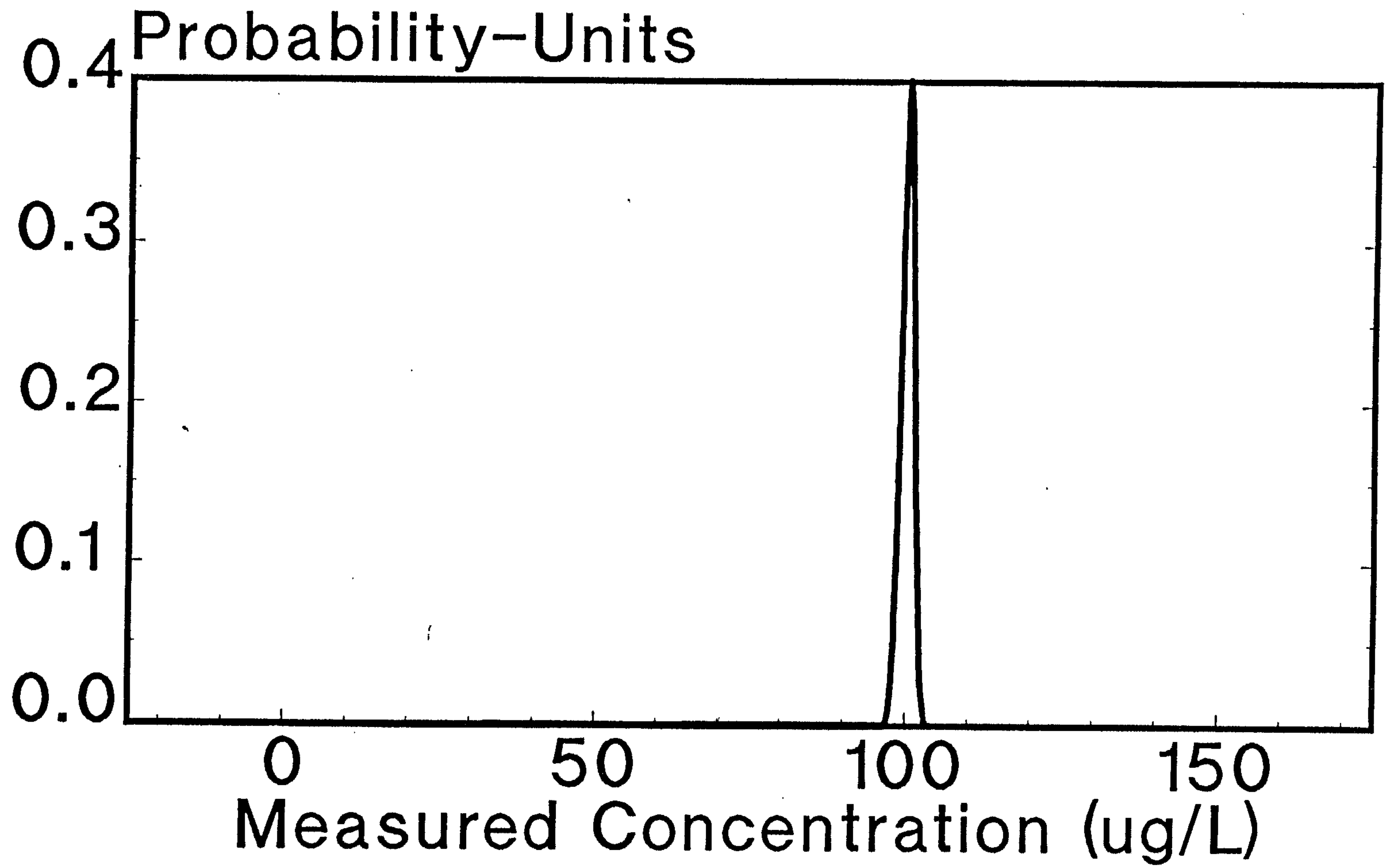

Figure 6. Normal Curve of Random Error
Mean = 100 ug/L; Sigma = 30 ug/L

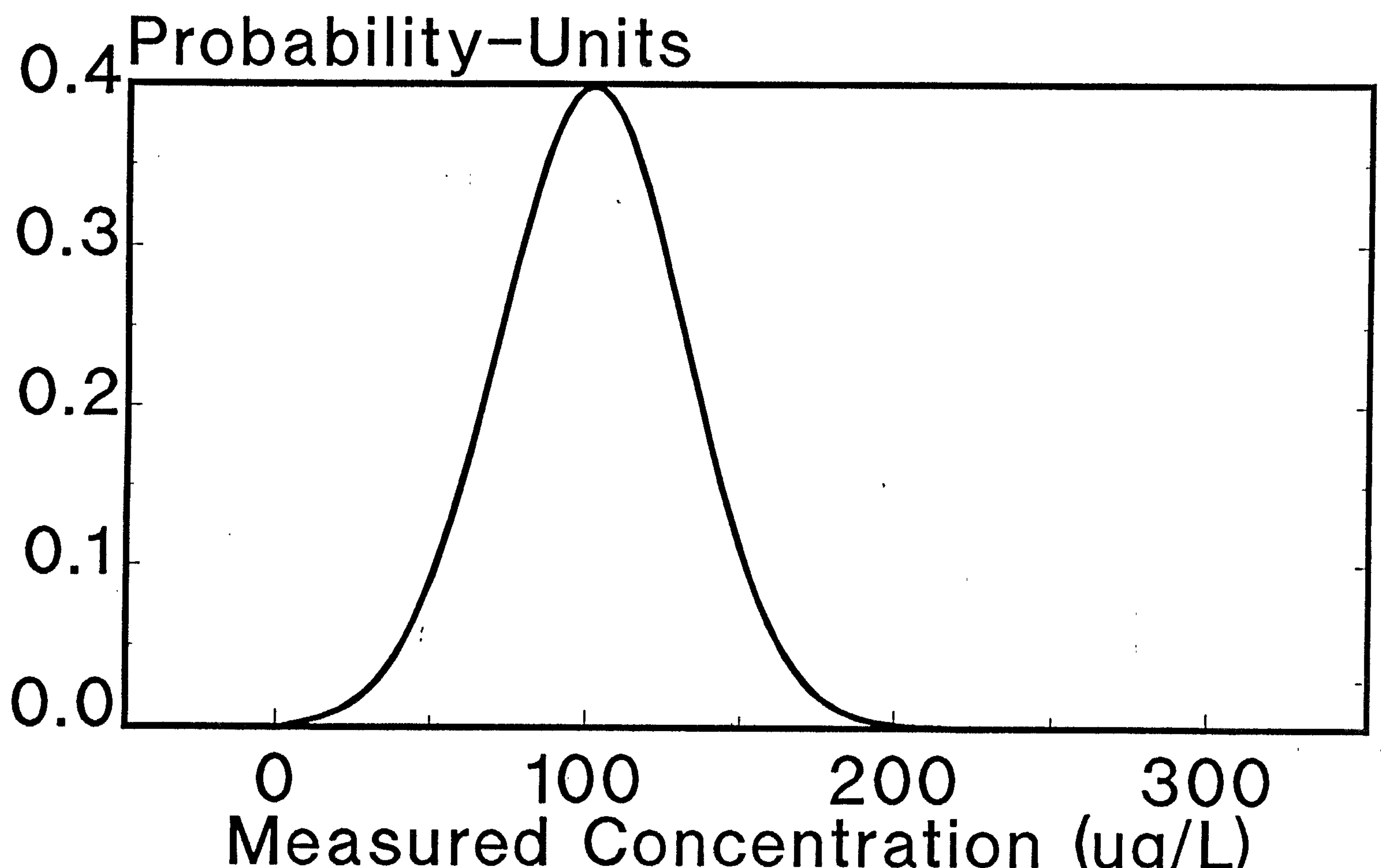

Figure 5. Normal Curve of Random Error
Mean = 100 ug/L; Sigma = 10 ug/L

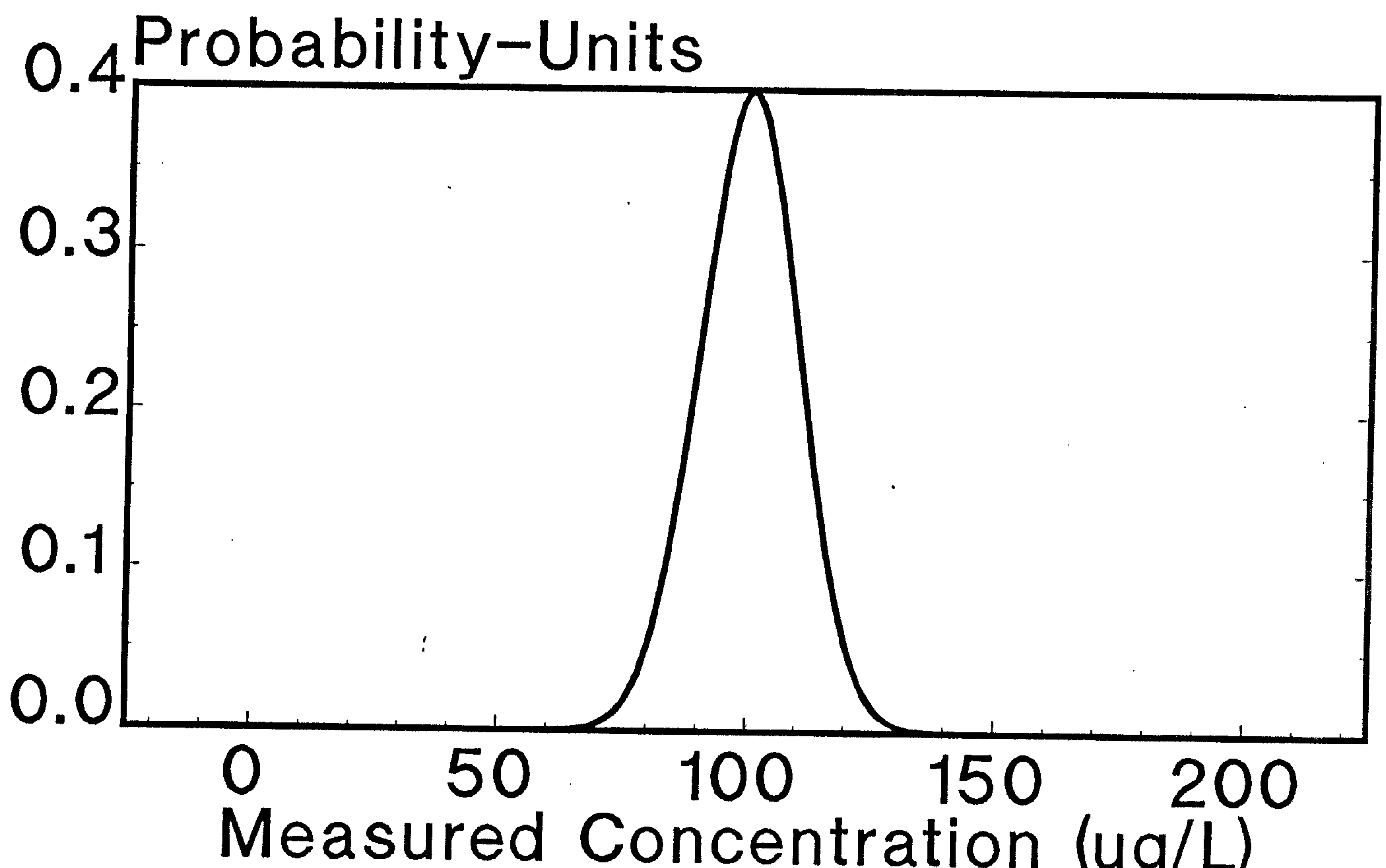

Figure 7. Normal Curve of Random Error
Mean = 100 ug/L; Sigma = 100 ug/L